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DEVELOPMENT OF X-RAY FLUORESCENCE
SPECTROSCOPY FOR ELEMENTAL ANALYSIS
OF PARTICULATE MATTER IN THE ATMOSPHERE
AND IN SOURCE EMISSIONS. PHASE II: EVALUA-
TION OF COMMERCIAL MULTIPLE CRYSTAL
SPECTROMETER INSTRUMENTS

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Naval Research Laboratory

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Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions

Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments

L. S. BIRKS AND J. V. GILFICH

*X-Ray Optics Branch
Nuclear Science Division*

June 15, 1973

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**Development of X-Ray Fluorescence Spectroscopy
for Elemental Analysis of Particulate Matter
in the Atmosphere and in Source Emissions**

**Phase II: Evaluation of Commercial Multiple
Crystal Spectrometer Instruments**

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Washington, D. C. 20375
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CONTENTS

Abstract	iv
Problem Status	iv
Authorization	iv
INTRODUCTION	1
EXPERIMENTAL RESULTS	4
DISCUSSION	6
Number of Elements	6
Tube Targets and Power	6
Crystals	6
Detectors	6
Data Handling	6
Sample Handling	7
REFERENCES	7

ABSTRACT

Four commercial multiple crystal spectrometer x-ray analyzers were evaluated for use in the elemental analysis of air pollution particulate samples. Fourteen to twenty-four elements can be measured simultaneously in these instruments. 100 second detection limits of 1 to 10 ng/cm² were achieved for about one-half of the elements examined. Any one of the commercial instruments is capable of performing quantitative analysis of the particulate matter filtered out of the atmosphere or source emissions. Some actual pollution samples were analyzed in all four instruments to demonstrate suitability.

PROBLEM STATUS

This report is the final report by the X-Ray Optics Branch on one phase of the problem; work is continuing on other phases of the problem.

AUTHORIZATION

NRL Problem P04-06

EPA-NRL Interagency Agreement No. 690114

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Manuscript submitted May 29, 1973.

**Development of X-Ray Fluorescence Spectroscopy
for Elemental Analysis of Particulate Matter
in the Atmosphere and in Source Emissions**

INTRODUCTION

In a previous report⁽¹⁾ it was concluded that multiple-crystal-spectrometers offer the most efficient method of performing large scale x-ray fluorescence analysis of air pollution particulate samples. Based on that conclusion, an investigation was inaugurated to evaluate the commercially available equipment of that type. Most large-scale industrial x-ray analysis is presently performed using these multiple crystal spectrometer instruments and there are four manufacturers of such equipment. Fourteen to twenty-four elements can be measured simultaneously. In addition to the combination of speed and resolution of these instruments a further advantage is that each spectrometer channel can be optimized for the individual element it is measuring (best divergence, best crystal, best detector). This is important for air pollution particulate samples where elements from sodium to lead must be measured. Table I lists the characteristics of the four commercial instruments as described in the manufacturer's literature.

TABLE I COMPARISON OF MULTICHANNEL INSTRUMENTS

	ARL <u>72000</u>	Rigaku <u>"SIMULTIX"</u>	Philips <u>PW 1270</u>	Siemens <u>MRS-3</u>
Max. No. of Spectrometers	24	24	14	17
No. of Positions Occupied by Scanner	3	3	Not Available	2
No. of Positions Occupied by Vac. Spectr.	All Vacuum	2	All Vacuum	All Vacuum
X-Ray Tubes Available	Machlett OEG-75 W, Pt, Rh-3 kW Cr-2.5 kW	Machlett OEG-75 W, Ag, Rh-3 kW Cr-2.5 kW	Philips FAA 100/3.5 Cr, Cu, Rh, Ag, Pt, Au- 3 kW; W, Mo-3.5 kW	Siemens AG-61 Mo, W, Au-3 kW Cr-2.6 kW Rh-1.5 kW
Crystal Optics	Curved and Ground	Flat	Flat	Logarithmic Curve
Read Out	Integrator	Integrator	Scaler	Scaler
X-Ray Incidence Angle	90°	90°	52°	45°
X-Ray Take-Off Angle	30°, 35°, 40°	30°	23°, 55°	30°, 38°, 52°, 60°

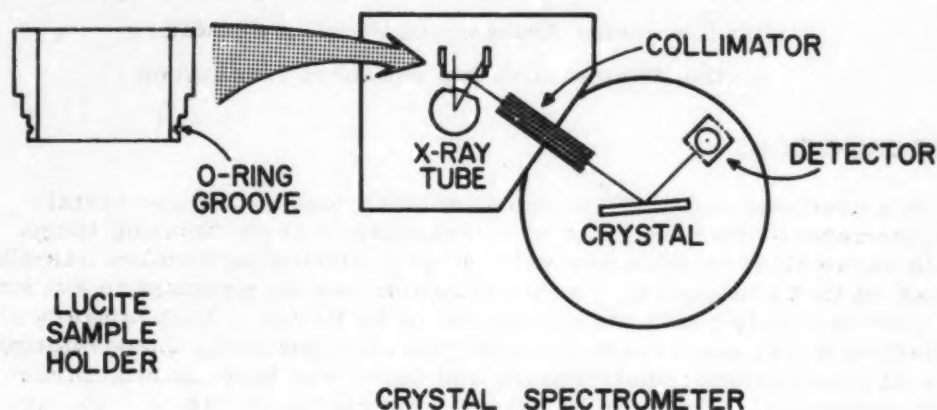


Figure 1. Geometry of the Laboratory Spectrometer

With the cooperation of the x-ray equipment manufacturers, sets of standards prepared at the Naval Research Laboratory (NRL) along with air pollution samples collected by the Environmental Protection Agency (EPA) were taken to each of the manufacturers' applications laboratory and measured by NRL personnel using the multiple spectrometer instruments.

As noted in the previous report, the most significant modification made to the laboratory equipment during the Phase I investigation was to design the sample holder so that primary radiation illuminated only the sample on its filter substrate and after being transmitted through the substrate, was trapped in an area which could not be viewed by the measuring system. This is illustrated for the laboratory wavelength dispersion spectrometer in Figure 1. One specific goal of the Phase II effort was to determine how the specimen holders of the commercial instruments could be similarly modified within the constraints imposed by their mechanical construction. All four of the instruments evaluated were amenable to the use of a sample cup as shown for a composite instrument in Figure 2. For the measurements reported here, three of the commercial instruments used plastic sample cups, while the fourth instrument used a gold-plated metal cup. Because these multi-channel instruments have the spectrometers arranged on an arc or circle around the sample, it was not possible to avoid having some of the spectrometers view a portion of the sample cup illuminated by the primary beam as shown in the figure. Therefore the background was not as low as might have been possible if more extensive modifications could have been made as shown in Figure 3.

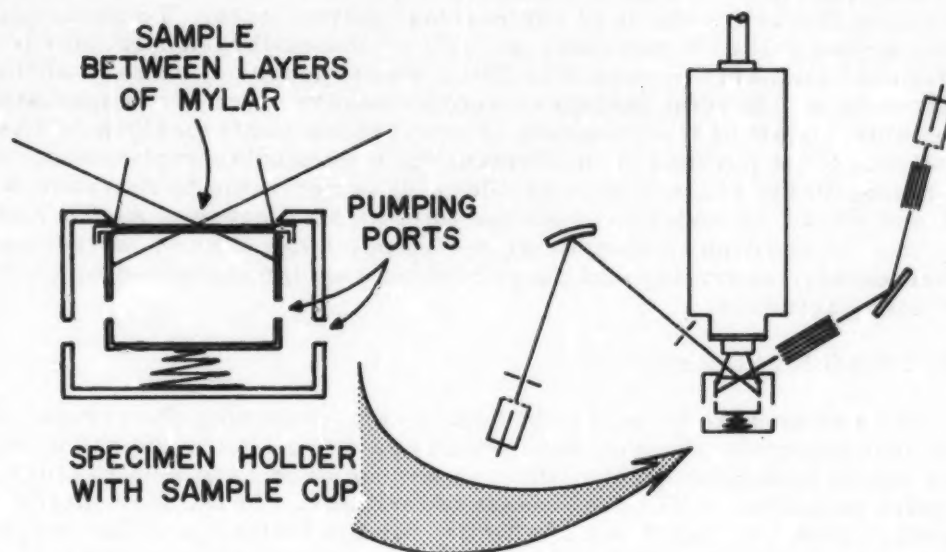


Figure 2. Geometry of a composite multiple spectrometer instrument, shown for an end-window x-ray tube and both curved and flat crystal x-ray optics. Side window tubes present an analogous situation.

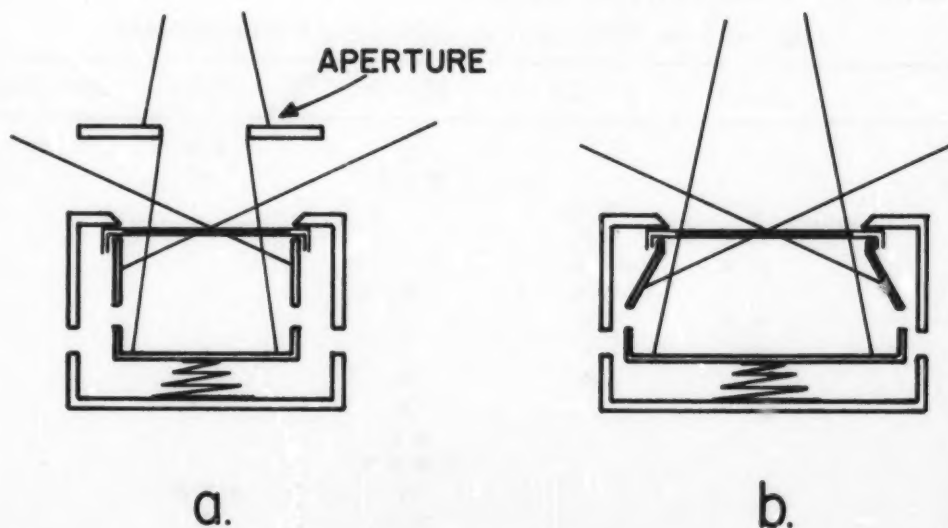


Figure 3. Modifications to the sample holder to decrease the background due to fluorescence and scattering of the primary x-ray beam.

- a.) Aperture
- b.) Large Sample Cup

Birks and Gilfrich

A second goal of Phase II was a comparison of the sensitivity and detection limits for the four commercial instruments. To accomplish this, actual pollution samples, as well as the calibration standards of individual elements prepared at NRL, were measured on each of the instruments. In some instances spectrometers were not immediately available for all of the elements of interest but presumably would be available for a purchased instrument for a particular application. For instance, in the air pollution problem, it is desirable to measure As $K\beta$ and Pb $L\beta$ in order to avoid the interference between As $K\alpha$ and Pb $L\alpha$. In addition to measuring the samples the ease of instrument disassembly, servicing and recalibration was demonstrated by each of the manufacturers.

EXPERIMENTAL RESULTS

In an attempt to be perfectly objective in reporting the results of this investigation, the only data which are being shown are the detection limits measured on the filter paper standards and some actual results on pollution samples measured with each of the four instruments. Table II lists detection limits for the elements of interest with the number of check marks in each range indicating the number of instruments giving detection limits within that particular range. The purpose of the somewhat cryptic presentation of data is to avoid giving the impression of endorsement to any individual manufacturer.

TABLE II 3σ DETECTION LIMITS
ng/cm² on Filter Paper (100 sec. measurement)

	1 - 5	5 - 10	10 - 50	50-200	200-500
Na				x x	x
Mg			x x x	x	
Al	x x	x x			
Si	x x	x x			
S	x x	x x			
Cl		x x	x		
K	x x	x			
Ca	x x	x			
V		x	x		
Fe			x	x x	
Co			x x		
Ni			x x x x		
Cu			x	x x x	
Zn			x x	x	
As ($K\beta$)				x	
Cd ($L\alpha$)	x			x	
Pb ($L\alpha$)			x x		

NRL Report 7617

TABLE III POLLUTION SAMPLES

Concentration ($\mu\text{g}/\text{cm}^2$)

	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Co	Ni	Cu	Zn	Cd	Pb
Incinerator C-7 NRL			0.63	0.35	20	100	21	1.4	0.05	2.5	0.30	ND*	2.5	58	0.33	59
Instrument A	13	0.14	0.40	0.14	10	84	6.6	0.93	0.02	1.6	0.05	0.23	2.1	78	0.37	55
Incinerator C-9 NRL			ND	ND	ND	3.6	0.04	0.24	ND	ND	ND	ND	ND	0.12	ND	ND
Instrument A	0.04	0.01	ND	0.02	0.10	2.2	ND	ND	ND	ND	ND	ND	ND	ND	0.002	ND
B	ND	ND	ND	ND	0.13	2.3	0.04	0.14	ND	0.11		0.01	ND	ND	ND	0.63
C	ND	ND	ND	0.03	ND	1.8	ND	ND			ND	0.08	ND	ND		
D		0.05	0.02	ND	0.003		ND			0.15		0.03	ND			0.07
Incinerator N-6 NRL			ND	0.30	63	70	15	2.0	ND	2.0	ND	0.30	5.0	120	ND	120
Instrument A	38	0.73	0.31	0.41	68	65	16	1.8	0.09	2.1	0.09	0.60	6.6	200	0.79	110
B	13	0.89	0.39	0.38	40	>56	51	2.0	1.2	2.0		0.08	2.6	90	3.1	86
C	30	1.7	0.34	0.95	88	73	48	1.9			ND	0.23	4.4	250		
D		2.6	0.31	0.37	76			2.0		5.7		0.39	5.1			130
Incinerator B-1 NRL			ND	0.08	3.2	17	3.5	0.30	ND	0.50	0.04	0.40	0.80	13	ND	4.4
Instrument A	6.0	0.04	0.15	0.08	2.1	16	1.0	0.19	ND	0.22	ND	0.20	ND	18	0.08	4.6
B	0.81	ND	0.17	0.09	2.6	15	3.6	0.31	0.11	0.23		0.01	ND	6.5	0.31	4.8
C	3.3	0.14	0.17	0.27	3.0	15	3.5	0.17			ND	ND	ND	16		
D		0.35	0.22	0.12	3.3			0.25		0.40		ND	0.29			4.2
Incinerator B-3 NRL			ND	1.1	14	33	10	4.9	ND	2.5	ND	0.40	1.7	37	ND	34
Instrument A	11	0.21	1.1	0.48	10	38	4.2	1.6	0.12	2.0	0.05	0.20	1.3	61	0.53	35
B	3.2	0.61	1.2	0.53	13	42	13	1.7	0.26	1.8		0.03	ND	21	1.2	34
C	7.6	0.75	1.6	1.4	17	40	15	1.6			ND	0.11	0.89	65		
D		1.3	1.4	0.53	17			1.8		4.8		0.14	1.0			37
Incinerator T-16 NRL			ND	0.30	8.1	1.8	2.5	0.40	ND	0.30	ND	0.30	0.90	13	ND	11
Instrument A	5.9	0.03	0.02	0.23	5.0	7.3	3.2	0.37	ND	0.28	ND	0.05	0.46	19	0.65	12
Incinerator T-17 NRL			1.1	0.60	20	5.3	6.7	1.5	ND	0.80	ND	0.50	2.0	32	ND	29
Instrument A	12	0.06	0.10	0.51	12	3.6	9.1	1.2	ND	0.81	ND	0.10	1.4	40	1.5	30
Power 12 NRL			6.2	8.6	21	ND	2.8	5.6	0.07	14	0.10	0.70	1.1	0.50	ND	1.0
Instrument A	0.73	0.45	8.7	7.6	16	ND	3.8	4.2	0.23	17	0.04	0.20	0.10	0.45	0.01	ND
B	0.52	0.83	11	9.0	17	ND	2.7	5.0	0.20	16		0.19	ND	0.22	0.41	ND
C	0.61	0.77	13	24	20	ND	2.6	4.5			0.04	0.21	ND	0.53		
D		1.0	12	9.4	21			5.0		37		0.30	0.51			0.14
Cement 1A-B(g) NRL			ND	0.03	0.30	0.30	0.06	0.20	ND	0.20	ND	0.40	0.80	0.30	ND	ND
Instrument A	0.06	ND	ND	0.004	0.21	ND	0.14	0.04	ND	ND	ND	ND	ND	ND		
Cement 4D-B(g) NRL			ND	0.10	0.30	0.70	0.20	0.50	ND	0.30	ND	0.30	1.0	0.30	ND	ND
Instrument A	0.12	0.04	0.03	0.16	0.27	0.38	0.28	0.66	ND	0.14	ND	ND	ND	ND	0.002	ND
Cement 1A-B(o) NRL			ND	0.20	0.30	0.60	0.20	0.90	ND	0.10	ND	0.20	1.0	0.20	ND	0.60
Instrument B	ND	ND	ND	0.20	0.20	0.67	0.13	0.32	ND	0.07		ND	ND	ND	ND	ND
C	ND	ND	0.03	0.47	0.27	0.10	0.17	0.31			ND	ND	ND	ND		
D		ND	0.06	0.20	0.40			0.45		0.24		0.03	ND			0.09

* ND = Not Detectable

Table III shows quantitative analyses for some of the EPA samples with the results coded so that the instruments are identified only as "A, B, C and D." Previous x-ray analyses at NRL are also shown. The overall estimates of concentration are similar from instrument to instrument but occasionally one element will appear low or high by more than a factor of two. Inasmuch as the calibration curves all showed deviation only within statistical limits⁽²⁾ the most logical speculation concerning these differences in results seems to be that the particles are not uniformly deposited and that different areas were examined by different instruments. There is no system to the discrepancies in terms of instrument, element, concentration or sequence of measurement.

DISCUSSION

The experimental results show that all four of the commercial instruments can measure the desired elements in the concentration range of interest for air pollution. Simple modification of the specimen holder to use a sample cup improved the detection limits to the range of 1 to 10 ng/cm² for almost half of the elements studied. More extensive modification, as illustrated in Figure 3, should improve this even further.

All of the instruments are convenient to operate and service; a relatively short period of time was required (about an hour or two) to change the x-ray tube, realign or replace a spectrometer or components thereof and to put the instrument back into operation.

Table I listed a comparison of the physical characteristics of the four commercial instruments, a discussion of which follows:

Number of Elements. The smallest number of elements which can be measured simultaneously is 14. Depending on the ultimate decision of EPA concerning the number of critical elements to be measured, this may or may not be adequate. A scanning spectrometer in addition to the fixed spectrometers would make it possible to analyze for additional elements. Under certain circumstances incorporation of an energy dispersion system would allow semiquantitative analysis of several additional elements.

Tube Targets and Power. All of the instruments can be equipped with an adequate selection of x-ray tubes operable at 2.5 kW or higher.

Crystals. Two of the instruments use curved crystals while the other two instruments use flat crystals. However, on the basis of the work reported here, there does not seem to be any compelling justification to consider one type of crystal more desirable than the other.

Detectors. All of the instruments use gas proportional counters or their equivalent and have similar efficiencies. However, only two instruments employ pulse amplitude discriminators on all channels. The ability to discriminate against higher order diffraction of shorter wavelengths is desirable in the pollution measurements because of the wide range of concentrations encountered and because of the requirement to minimize the background. Therefore it seems necessary that pulse height analyzers be used on all channels.

Data Handling. Two of the instruments use scaler circuits to read out the number of x-ray photons collected by each channel whereas the other two use the detector output to charge a capacitor and then read the integrated charge as intensity. The scaler read-out is somewhat more readily interpreted statistically but this is relatively unimportant.

NRL Report 7617

The capacitors do have one undesirable feature, however, namely a limited amount of charge can be accumulated. Thus it must be decided in advance what instrument multiplier to use so that the charge is large enough to be easily readable but not so large that the integrator saturates. Although this may be a minor difficulty in many cases, the fact that it can be troublesome does, to some extent, indicate the desirability of using scalers.

Sample Handling. All of the instruments were modified by using a sample cup to support the filter and reduce the scattered background, as was illustrated in Figure 2. This is necessary in order to achieve the detection limits listed in Table II. If EPA should implement tentative plans to use rolls of filter-paper tape or frame-mounted filters for sampling, automatic sample handling could be expected to improve the efficiency of the analyses. The manufacturers of all four instruments have indicated a willingness to consider such an automated sample-handling system. In fact, some of the instruments have designs for sample-handling devices which can process up to 160 samples without operator attention or, in some cases, provide for the analysis of samples as fast as they can be prepared by automated ancillary equipment from a process stream.

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¹"Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," L. S. Birks, J. V. Gilfrich and P. G. Burkhalter, Environmental Protection Agency Report R2-72-063, Oct. 1972.

²L. S. Birks, X-Ray Spectrochemical Analysis, 2nd ed., Wiley-Interscience, New York, 1969, pp. 80-82.